

## III.A.10 Quantitative Characterization of Chromium Poisoning of Cathode Activity

### Objectives

- Develop *in-situ* chemical mapping techniques to measure the accumulation of chromium (Cr) chemical species at the cathode of an operating solid oxide fuel cell (SOFC).
- Prepare SOFC cathode samples with controllable amounts of electrode and electrolyte surfaces as well as cathode-electrolyte interfaces that are easily accessible to *in-situ* electrochemical and optical (Raman) characterization techniques.
- Correlate Cr contamination delivered by vapor phase Cr-containing molecules and the electrochemical charge transfer resistance of the cathode.
- Deduce the mechanism for Cr poisoning of the SOFC cathode.

### Accomplishments

- Measured the Raman detection limit of  $\text{Cr}_2\text{O}_3$  thin films on the surface of a lanthanum strontium manganese (LSM) cathode. Without additional enhancement methods, accumulations as thin as 10 nm can be detected.
- Created LSM/gadolinia-doped ceria (GDC) composite electrode samples with quantifiable cathode/electrolyte interfaces suitable for our *in situ* Raman measurements. Also fabricated samples with micron-scaled patterned LSM electrodes (with precise geometries) deposited on yttria-stabilized zirconia (YSZ) substrates.
- Generated a surface enhanced Raman signal (SERS) effect on LSM and  $\text{Cr}_2\text{O}_3$  films by co-depositing silver nanoparticles within the film using combustion chemical vapor deposition (CCVD).

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Signal enhancement factors between 5 and 1000 were obtained.

- Fabricated silver-coated atomic force microscopy (AFM) tips with diameters as small as 30 nm to be used for generating tip enhanced Raman signal (TERS) effects to obtain sub-micron resolution of surface Raman mapping.

### Introduction

One primary suspected cause of long-term performance degradation of SOFCs is the accumulation of Cr species at or near the cathode/electrolyte interface due to reactive Cr molecules originating from Cr-containing components (such as the interconnect) in fuel cell stacks. To date, considerable efforts have been devoted to the characterization of cathodes exposed to Cr sources; however, little progress has been made because a detailed understanding of the chemistry and electrochemistry relevant to the Cr-poisoning processes is still lacking. This project applies multiple characterization methods – including various Raman spectroscopic techniques and various electrochemical performance measurement techniques – to elucidate and quantify the effect of Cr-related electrochemical degradation at the cathode/electrolyte interface. Our chosen methods and unique experimental setup allow for direct spectroscopic observation of the Cr poisoning process while simultaneously monitoring performance degradation of an operating cell. The study will establish the scientific basis for achieving rational design of Cr-tolerant cathode materials and structures for low-temperature SOFCs with Cr-based interconnect materials.

### Approach

This project centers around coupling standard electrochemical performance measurements with our unique *in situ* Raman spectroscopy experimental setup to map the concentration of Cr-containing species on the electrode surface as a function of cell operating conditions. Raman spectroscopy identifies the various chemical species in the system by measuring the way in which the sample scatters an incident laser light signal. By using a microscope and motorized stage to direct the laser light, we can map the chemical environment on and around the cathode/electrolyte interface. To more easily probe this interface, composite cathode surfaces (primarily GDC/LSM) are constructed with dense,

well-defined surface structures, and the boundary length vs. surface area are quantified with scanning electron microscopy (SEM). The performance of the cathode under different operating conditions is measured using electrochemical impedance spectroscopy (EIS) while simultaneously monitoring the distribution of Cr species deposited on the cathode surface using Raman mapping. The kinetics of Cr mass transport and deposited surface structures will be determined relative to its effect on electrochemical performance at various temperatures, polarizations, and atmospheres.

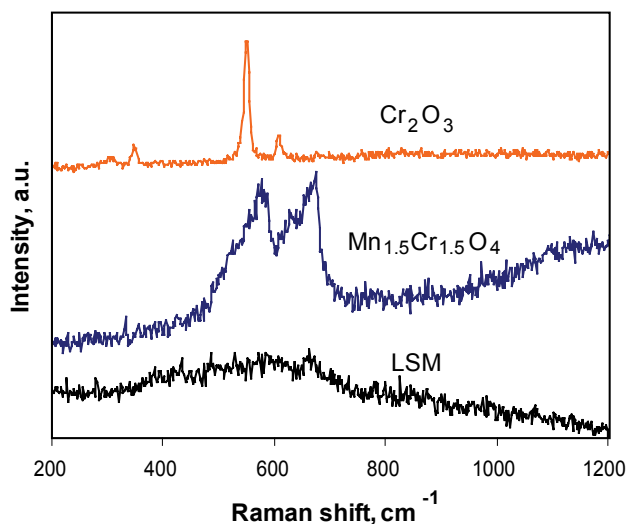
In order to detect extremely small amounts of Cr species on the surface, the Raman signal can be enhanced through either deposition of metal nanoparticles on the cathode surface (surface enhanced Raman signal, or SERS) or by bringing a nano-sized metal scanning tip near the cathode surface (tip enhanced Raman signal, or TERS). The increased sensitivity through SERS or TERS methods will allow for earlier detection of deposited Cr species on the sample. The *in situ* Raman data will be verified using various *ex situ* characterization methods including scanning Auger mapping (SAM), X-ray photoelectron spectroscopy (XPS), and further Raman measurements.

## Results

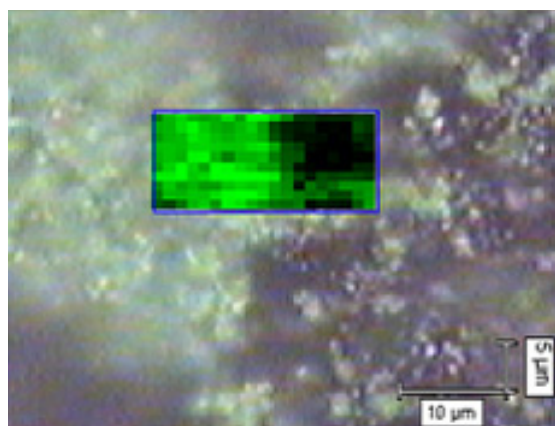
The first round of Raman measurements involved demonstrating the utility of normal Raman spectroscopy (measurements without signal enhancements) with respect to Cr contamination of an LSM cathode. As shown in Figure 1, the Raman signals from possible chromium containing contaminants are different from that of the LSM cathode, meaning Raman spectroscopy can indeed distinguish between the multiple species present. For example, the sharp peaks at  $350\text{ cm}^{-1}$  and

$550\text{ cm}^{-1}$  in the spectrum of  $\text{Cr}_2\text{O}_3$  can be used as a marker in contrast with the relatively flat spectrum of the LSM. For each desired species, an algorithm has been created to quantify the intensity of the Raman signal from the specific species so that Raman maps can be created from our samples that plot the Raman signal from the species as a function of position. Figure 2 shows an example of a Raman map of  $\text{Cr}_2\text{O}_3$  from a sample containing a mixture of  $\text{Cr}_2\text{O}_3$  and LSM. The spatial resolution of the map is on the order of  $2\text{ }\mu\text{m}^2$ .

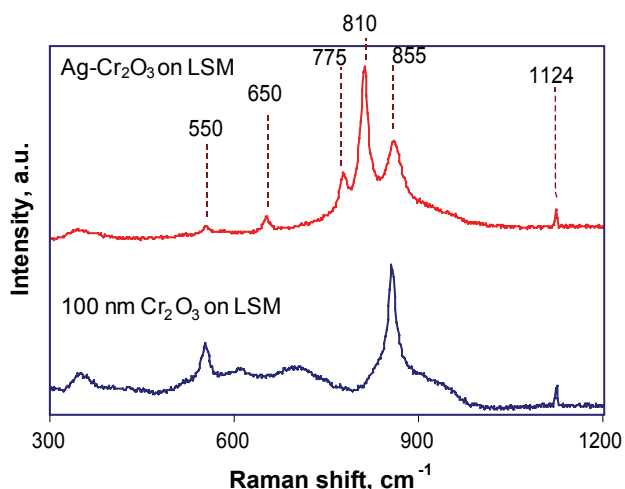
The sensitivity of the Raman microscope to the presence of  $\text{Cr}_2\text{O}_3$  was then determined by sputtering thin  $\text{Cr}_2\text{O}_3$  films of varying thicknesses onto LSM samples and measuring the Raman signal. Films as thin as 10 nm could be detected, even without signal enhancements. Further, a calibration curve was obtained to correlate the Raman signal from the  $\text{Cr}_2\text{O}_3$  film to its thickness. To detect extremely thin layers of  $\text{Cr}_2\text{O}_3$  ( $< 10\text{ nm}$ ), we have attempted incorporation of Ag or Au nanoparticles into the cathode, which has been shown to increase the Raman signal from the volume around the nanoparticles through a phenomenon known as the SERS effect. The nanoparticles have been introduced so far through two different methods: (1) the evaporation of Ag or Au colloids placed on the cathode surface, leaving behind the nanoparticles within the colloid, and (2) the co-deposition of Ag nanoparticles with the cathode upon an electrolyte substrate using CCVD. Both of these methods have produced varying degrees of success, increasing the Raman signal from LSM or  $\text{Cr}_2\text{O}_3$  by a factor between 5 and 1000, depending on the technique and the material. Specific peaks within a given Raman spectrum are enhanced by different amounts, and previously undetected peaks have also appeared with the addition of the metal nanoparticles. Figure 3 shows the SERS effect generated from a  $\text{Cr}_2\text{O}_3$  film that was prepared by CCVD with and



**FIGURE 1.** Raman spectrum of LSM cathode compared to those of  $\text{Cr}_2\text{O}_3$  and  $\text{Mn}_{1.5}\text{Cr}_{1.5}\text{O}_4$  powders.



**FIGURE 2.** Raman map (overlaid on top of an optical micrograph) showing the presence of  $\text{Cr}_2\text{O}_3$  on the surface of a dense LSM cathode. A brighter shade of green indicates a stronger  $\text{Cr}_2\text{O}_3$  signal.

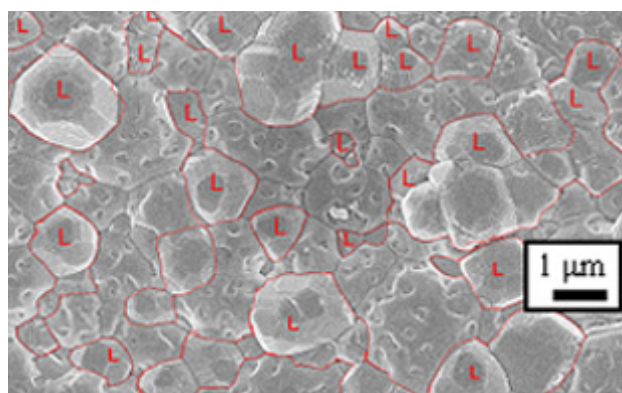


**FIGURE 3.** Raman spectra from  $\text{Cr}_2\text{O}_3$  films deposited by CCVD with and without Ag nanoparticles onto an LSM substrate.

without the presence of Ag nanoparticles. Ongoing experiments and theoretical calculations are being undertaken to standardize the methods used to generate the SERS effects and to account for the presence of new peaks in the spectra.

Work has also been completed towards increasing Raman sensitivity through the TERS effect. Instead of placing metal nanoparticles directly on the cathode surface, a silver-coated AFM tip is brought within a few nanometers of the cathode surface, close enough to obtain a signal enhancement effect. To this end, we finalized a process for manufacturing silver-coated tungsten tips with diameters ranging from 30 to 300 nm. We are currently integrating the AFM control apparatus with our Raman experimental chamber so that we can measure the ability of these tips for creating a significant TERS effect.

To perform Raman mapping around the cathode/electrolyte interface, we created samples consisting of GDC/LSM composites with dense sample surfaces consisting of regions of LSM and GDC large enough to be able to effectively distinguish between the two phases within the spatial resolution of our Raman microscope. The triple phase boundary (TPB) per unit area between the LSM, GDC, and air has been quantified statistically using SEM micrographs. Figure 4 shows a typical composite sample surface. These composite samples are currently being used in our ongoing *in situ* Raman mapping experiments. The samples are subjected to normal SOFC operating conditions and exposed to Cr-containing vapor while simultaneously monitoring the performance of the sample and collecting Raman spectra from the surface.



**FIGURE 4.** SEM micrograph of LSM/GDC composite surface. The red lines indicate the TPB between the GDC, LSM, and air. Grains labeled with an 'L' are LSM.

## Conclusions

- Even without signal enhancement, Raman mapping of Cr-containing species can be performed on SOFC cathodes for deposits thicker than 10 nm.
- A SERS effect from LSM and  $\text{Cr}_2\text{O}_3$  can be generated by depositing silver nanoparticles on the sample surface.
- Raman spectroscopy (including SERS and TERS) has the potential for *in situ* probing and mapping of Cr species deposited on cathode surfaces in a functional SOFC under practical operating conditions.

## Future Directions

- Continue *in situ* Raman mapping experiments to measure deposition of Cr species around the cathode/electrolyte interface.
- Incorporate TERS measurements into *in situ* and *ex situ* characterization of Cr-contaminated cathode surfaces to increase the sensitivity of our Raman measurements.
- Correlate the distribution of Cr species (as determined by Raman mapping) with the electrochemical performance (as determined by impedance spectroscopy) of cathodes in operating SOFCs to understand the mechanism of Cr poisoning.
- Design and fabricate cathodes of improved tolerance to Cr contamination.

**FY 2006 Publications/Presentations**

1. H. Abernathy, Y. Choi, S. Zha, Z. Cheng, J. Wang, R. Das, E. Koep, R. Williams, J. Dong, M. Liu, "Recent Progress in Understanding Interfacial Reactions in SOFCs", Presented to The 30th International Conference on Advanced Ceramics and Composites (American Ceramic Society), Cocoa Beach, FL, January 2006.
2. H. Abernathy, J. Dong, S. Choi, and M. Liu, "In Situ Probing and Mapping of  $\text{Cr}_2\text{O}_3$  Deposition on LSM-Based Cathodes in SOFCs", in preparation.
3. J. Dong, R. Williams Jr., H. Abernathy, and M. Liu, "Characterization of Chromium Poisoning of SOFC's Cathodes", Symposium for the Georgia Tech Strategic Energy Initiative, Atlanta, GA (2006).